FINAL REPORT

Brown University

DA Project No. 20010501B700

Contract No. DA-31-124-ARO(D)-163

Detailed Studies of Chemical Reaction Kinetics

8 October 1967

by

E.F. Greene and J. Ross

Requests for additional copies by Agencies of the Department of Defense, their contractors, and other Government agencies should be directed to:

Armed Services Technical Information Agency
Arlington Hall
Arlington 12, Virginia

Department of Defense contractors must be established for ASTIA services or have their "need-to-know" certified by the cognizant military agency of their project or contract.

All other persons and organizations should apply to the:

U.S. Department of Commerce
Office of Technical Services
Washington 25, D.C.

For the past four years at Brown University the Advanced Research Projects Agency has been supporting research directed toward providing a clearer understanding of the details of the kinetics of chemical reactions. The purpose of this research has been to find out more exactly how chemical reactions occur. The work has been both theoretical and experimental, involving molecular beam and shock wave techniques.

The major part of the experimental work has been directed to measuring the scattering of velocity selected beams of alkali metal atoms by crossed beams of various target molecules, both reactive and non-reactive ones. The direct, experimental results are differential cross sections for non-reactive scattering which can be interpreted to yield: (for all systems studied)
1) Numerical values of parameters in an assumed form of the interaction potential for the reactants; and(for the reactive systems)
2) the probability of reaction as it varies with impact parameter or the potential energy at the distance of closest approach during a collision; 3) the magnitude and energy dependence of the total reaction cross section; 4) threshold energies for reaction and the maximum distance of separation of the reactants for which reaction can occur. These results have been obtained from studies of potassium scattered by HCl, HBr, DBr, HI, CH_3Br, CH_3I, CCl_4, CBr_4, $SiCl_4$, $SnCl_4$, SF_6, $C(CH_3)_4$, $(CH_3)_2C=C(CH_3)_2$, benzene, and cyclohexane, Br_2, adamantane, $(CH_3)_3CBr$, $\emptyset_3CBr$, and $(NC)_2C=C(CN)_2$ and of Cs scattered by HBr. The more reactive systems such as K + $SnCl_4$ or SF_6 have reaction cross sections of the order of 10^2 $\AA^2$. These remarkably large values show that chemical reaction can not always be considered a small perturbation on elastic scattering.

Other experiments have been carried out with an Ar atom beam in a higher energy range (20-200eV). The fast beam is produced by ionization of Ar followed by acceleration and then neutralization of the ions. This beam has been used for studies of the reaction $Ar + CsF \rightarrow Ar + Cs + F$ (for which no products were detected above the noise level) and $Ar + Ar \rightarrow Ar^+ + Ar + e$. Results from this kind of experiment help to clarify the nature of the interactions of atoms at these higher energies.

An apparatus has been built for the study cross sections for inelastic transitions. An alkali beam passes through a velocity selector, is scattered by a cross beam, and is velocity analyzed before detection. Clear cut measurements of energy transfer between translation and internal energy on collision should soon become possible.

An experiment with similar objectives was carried out in a shock tube with the system HI diluted with Ar. The rate of energy transfer from translation to the three lowest vibrational quantum states of HI was measured. The exchange of vibrational quanta between HI molecules apparently occurs with a high probability. Other shock tube experiments have helped to show how two Br atoms, produced from heating Br_2 or HBr, may recombine on collision with the emission of a photon.

The theoretical work has also been directed toward providing a clearer understanding of the nature of inelastic and chemically reactive collisions. Particular results have been 1) a theoretical justification of the empirical method used for interpreting the

data from the nonreactive scattering experiments, 2) a semi-classical theory for the rotational excitation of a diatomic molecule by an atom, 3) a quantum mechanical calculation of a reaction cross section for K + HBr, 4) an application of R-matrix theory for the derivation of both an activated complex theory and a statistical theory of chemical reaction rates, and to resonances expected in low energy elastic scattering, 5) evaluation of scattering cross sections in the optical model. These results help not only in understanding the experimental results but also in showing what new experiments may be useful.

Publications

1. M. Ackerman, E.F. Greene, A.L. Moursund and J. Ross, "Elastic and Reactive Scattering of K by HCl and HI in Crossed Molecular Beams", J. Chem. Phys. 41, 1183 (1964).

2. E.F. Greene, A.L. Moursund and J. Ross, "Elastic Scattering in Chemically Reactive Systems", Adv. Chem. Phys. 10, 135 (1966).

3. C.C. Chow and E.F. Greene, "Vibrational Relaxation of HI, 1400° - 2300° K," J. Chem. Phys. 43, 324 (1965).

4. J.L.J. Rosenfeld and J. Ross, "Calculation of Chemical Reaction Probabilities from Elastic Scattering Data", J. Chem. Phys. 44, 188 (1966).

5. K.P. Lawley and J. Ross, "Semiclassical Theory of Rotational Excitation of a Diatomic Molecule by an Atom", J. Chem. Phys. 43, 2920 (1965).

6. K.P. Lawley and J. Ross, "Semiclassical Calculation of Rotational Excitation," J. Chem. Phys. 43, 2943 (1965).

7. B.C. Eu and J. Ross, "Some Applications of the R-Matrix Theory to Reactive and Elastic Molecular Scattering," J. Chem. Phys. 44, 2467 (1966).

8. B.C. Eu and J. Ross, "Comments on Two Derivations of a Transition-State Theory of Chemical Reactions, J. Chem. Phys. 46, 411 (1967).

9. J.R. Airey, E.F. Greene, K. Kodera, G.P. Reck and J. Ross, "Nonreactive Scattering of K by HBr and DBr in Crossed Molecular Beams," J. Chem. Phys. 46, 3287 (1967).

10. J.R. Airey, E.F. Greene, G.P. Reck and J. Ross, "Scattering of Potassium by a Series of Reactive and Nonreactive Compounds in Crossed Molecular Beams", J. Chem. Phys. 46, 3295 (1967).

11. H.Y. Sun and J. Ross, "Evaluation of Scattering Cross Sections in the Optical Model by the Method of Stationary Phase", J. Chem. Phys. 46, 3306 (1967).

12. E.F. Greene, G.P. Reck and J.L.J. Rosenfeld, "Analysis of Elastic-Scattering Data in the Semiclassical Approximation," J. Chem. Phys. 46, 3693 (1967).

Ph.D. Theses

1. C.C. Chow, "Vibrational relaxation of gaseous hydrogen iodide behind a shock wave", June 1964.

2. A.L. Moursund, "The elastic and reactive scattering of K by HCl, CH_3Br, and HI in crossed molecular beams", July 1964.

3. C.H. Williams, Jr., "The dissociation of a cesium fluoride molecule by impact with a fast argon atom", July 1964.

4. R.J. Suplinskas, "Calculation of the chemical reaction cross section; K + HBr", June 1965.

5. B.C. Eu, "R-matrix theory for elastic and reactive molecular scattering", June 1966.

Scientific Personnel Supported

Graduate students (degrees received, if any)

C.C. Chow (Ph.D. 1964)
B.C. Eu (Ph.D. 1966)
R. Hammond
M.H. Lau
M.W. Lee
A.L. Moursund (Ph.D. 1964)
R.J. Suplinskas (Ph.D. 1965)
T.C. Wang
K. Westberg
C.H. Williams, Jr. (Ph.D. 1964)

Postdoctoral research associates

J.R. Airey
J.M.S. Henis
L.F. Hoffman
K. Kodera
K. Lawley
S. Miyazaki
G.P. Reck
J.L.J. Rosenfeld

Principal investigators

E.F. Greene
J. Ross

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*
Brown University

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b GROUP
NA

3. REPORT TITLE
DETAILED STUDIES OF CHEMICAL REACTION KINETICS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Final Report

5. AUTHOR(S) *(Last name, first name, initial)*
Greene, E. F.
Ross, J.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
8 Oct 67	5	

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
DA-31-124-ARO(D)-163	
b. PROJECT NO. ARPA ORDER NO. 501	
c. 20010501B700	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* 4676.7-C
d.	

10. AVAILABILITY/LIMITATION NOTICES
Distribution of this report is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
None	U.S. Army Research Office-Durham Box CM, Duke Station Durham, North Carolina 27706

13. ABSTRACT

For the past four years at Brown University the Advanced Research Projects Agency has been supporting research directed toward providing a clearer understanding of the details of the kinetics of chemical reactions. The purpose of this research has been to find out more exactly how chemical reactions occur. The work has been both theoretical and experimental, involving molecular beam and shock wave techniques.

14. KEY WORDS
molecular beam techniques
shock wave techniques
chemical reactions
alkali metal atoms
crossed beams

DD FORM 1 JAN 64 1473

Unclassified
Security Classification